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METHODS FOR MANUFACTURING AND DEPOSITING FINE PARTICLES COMBINING FLAME AND LASER BEAM

Technical Field

5   The present invention relates to a method for manufacturing fine particles including ceramic particles, metallic particles, glass particles or composite particles and a method of depositing the fine particles on a silica rod or wafer using a flame, and more particularly, to a method for controlling the size, morphology, phase and composition of fine particles produced in a flame combining a laser beam.

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Background Art

       FIG. 1 schematically shows an apparatus for flame hydrolysis deposition (FHD) for generating and growing particles in a flame. Referring to the drawing, gases such as N_2 are introduced into containers 1a and 1b containing the reactants to

15   then be carried to a burner 4. The reactants carried to the burner 4 are injected into a flame 5 generated by combustion of a fuel such as H_2 to thereby generate particles 6. The containers 1a and 1b containing the reactants, and the burner 4 are connected to each other by conduits, and valves 3 and mass flow controllers (MFCs) 2 are installed along the flow paths.

20   The reactants used in the apparatus vary according to a material to be manufactured, and multi-component composite particles may be produced using a plurality of reactants. For example, in the case of manufacturing an optical waveguide film or an optical fiber preform, reactants such as $SiCl_4$, $GeCl_4$, or $POCl_3$ are used. Since these reactants have a low vapor pressure at room temperature, their

25   flows are accurately adjusted by the MFCs 2 to then be supplied to the burner 4 via a carrier gas. The reactants injected from the nozzle of the burner 4 react with H_2O generated in the flame 5 due to combustion of hydrogen to thereby generate particles 6 such as SiO_2, GeO_2 or P_2O_5. These particles 6 are deposited on a target substrate 10.

30   In the case of manufacturing an optical fiber preform, the carrier gas for the reactants is replaced with oxygen, a silica rod (not shown) is installed, instead of the

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target substrate 10 and rotated at a speed of about 60 rpm, and the burner 4 is made to reciprocate left and right so that the generated particles are adhered to the silica rod. This is referred to as an outside vapor deposition (OVD) method. Also, in the case of manufacturing a planar optical waveguide film or an optical splitter using the

5   FHD method, a silicon wafer (not shown) is installed instead of the target substrate 10, and the wafer or the burner 4 is moved in a two-dimensional direction for deposition of particles.

In both cases, the most influential factors in the optical characteristics of a finally produced optical device and sintering characteristics of a preform, are the

10   size, composition and morphology of particles at the time of deposition.

Also, in the case of manufacturing a thin film by manufacturing fine powders such as ceramic nanoparticles, metallic nanoparticles or composite nanoparticles and then sintering the same, the formation of aggregates and the nonuniform distribution in the size of nanoparticles affects powder flow and packing, thereby forming porous

15   pores, which adversely affect the mechanical strength, optical and magnetic characteristics of the device. Further, in the case of manufacturing the fine powders having their own solid-state phases (for example, TiO_2 powders have three phases of anatase, brookite and rutile), the phases are differently favored according to their applications. Examples of applications currently being investigated include catalytic

20   materials, sensors, thin-film batteries and capacitors for electrical storage. As an example, TiO_2 has proved to be the most active photocatalyst for the treatment of toxic and biologically persistent compounds, with the anatase phase showing higher activity than rutile phase. Thus, in order to increase the quality and reliability in manufacturing various kinds of fine powders and an optical device using the fine

25   powders, it is important to form the particles having uniform size distribution and a spherical shape while being as small as possible in the nanometer scale and also to control the phase of fine crystalline powders. Thus, studies into solutions of these problems are critical issues in the art.

Burners which are currently used in manufacturing various kinds of fine

30   powders and optical devices include a coflow diffusion flame burner, a counterflow diffusion flame burner, a coflow premixed flame burner and so on. Depending on

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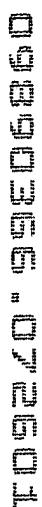
the type of burner, the temperature distribution and flow conditions vary considerably. However, the nucleation and growth mechanisms are basically the same as one another. The particle size and morphology are determined by the ratio of coalescence time of the particles to interparticle collision time of the particles (see

5   Y. Xiong et al., 1993, J. Aerosol Sci., 24(3), pp. 301-303 and S.E. Pratsinis, 1988, Prog. Energy Combust. Sci., 24, pp. 197-219.). If coalescence occurs faster than collision, that is, if the flame temperature is relatively high, as shown in FIG. 2A, two or more particles connected to one another coalesce to form an isometrically spherical particle. On the other hand, if collision occurs more frequently than

10   coalescence, as shown in FIG. 2B, particles are connected to one other like linear chains to form aggregates, instead of forming a sphere due to coalescence.

Here, the time required for the aggregate volume to double, as shown in FIG. 2B, is defined as the characteristic collision time (τ_c), which can be written in the following formula (see R. S. Windeler et al., 1997, Aerosol Sci. and Tech., 27, pp.

15   174-190.):

$$\tau_c = 2v^{3/2-2/D_f} \, (\frac{6kT}{\rho})^{-1/2} (\frac{3}{4\pi})^{1/2-2/D_f} (\frac{d_p}{2})^{6/D_f-1} (\alpha\phi)^{-1} \, ...(1)$$

where v is the average volume of aggregates, k is the Boltzmann constant, T is the temperature, ρ is density, α is a constant depending on Df, d_p is a diameter of an individual primary particle constituting an aggregate, ϕ is the volumetric ratio of

20   generated particles, that is, the ratio of a volume of generated particles to a volume of chemical carrier gases, and Df is the fractal dimension of aggregates. A Df value closer to 3 means that aggregates are substantially spherical, and a Df value closer to 1 means that aggregates are formed like linear chains. In the case of aggregates manufactured using a flame, the Df value ranges from 1.6 to 2.0.

25   Here, as the volumetric ratio ϕ increases, that is, as the amount of chemical materials is increased to enhance the deposition efficiency of particles or production rate of powders, the collision time becomes smaller than the coalescence time. Thus, a large aggregate is unavoidably formed due to collision among aggregates.

Also, the time required for two spherical particles to completely coalesce to

30   form an isometric sphere, as shown in FIG. 2A, is defined as the characteristic

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coalescence time (τ_f), which is largely classified into a solid state diffusion mechanism and a viscous flow mechanism according to the sintering mechanism of the particles. For example, TiO_2 particles go with the solid state diffusion mechanism and SiO_2 particles go with the viscous flow mechanism. The

5 characteristic coalescence time of SiO_2 can be written as the following formula (2) (see W.D. Kingery et al., 1976, Introduction to Ceramics, Wiley-Interscience, New York.):

$$\tau_f = 6.5 * 10^{-15} d_p \exp(\frac{8.3 * 10^4}{T}) \ldots (2)$$

Currently, various kinds of attempts are being made to control the particle

10 size. First, in the passive method which has been widely used to date, a fuel introduced into a burner, an oxidizer, the flow rate of a reactant carrier gas and the like are optimized. However, according to this method, in the case where the flow rate of a reactant carrier gas is high, the size of primary particles becomes smaller, but large-sized aggregates are produced. On the other hand, in the case of a low

15 flow rate at the same flame temperature, it is possible to produce spherical particles but the particle size increases to over 100nm. Furthermore, even if the fuel introduced into the burner and the injection positions of an oxidizer and a carrier gas are adjusted, it is difficult to produce independent spherical particles in a nanometer scale for large concentrations (see S.E. Pratsinis et al., 1996, Powder Tech., 86, pp.

20 87.).

Alternative method for controlling the particle size is to actively reduce the particle size by suppressing collision by directly applying a force to the particles, as shown in FIG. 3. In other words, since the particles produced using the flame of a burner 4 are electrically charged, when a strong direct-current (DC) electrical field

25 is applied to the particles by electrodes 11a and 11b at both sides, positively or negatively charged particles move to oppositely charged electrodes due to the electrical field. Thus, since the residence time of the particles in a high-temperature region of the flame is reduced and thus the coalescence rate of particles is reduced, the sizes of primary particles become smaller. Also, since charged particles move

30 from the flame to oppositely charged electrodes, which reduces the number density

of the particles in the flame, the collision rate among particles is reduced so that the sizes of aggregates become smaller. According to this method, the sizes of both primary particles and aggregates are made smaller. However, it is not possible to avoid collision due to turbulence generated by the movement of the particles to both

5   electrodes. Thus, even though the particle size is reduced, the formation of aggregates is unavoidable for the manufacture of high concentration aerosols. Also, since the produced particles are adhered to electrodes, the particle deposition efficiency is undesirably lowered (see S. Vemury et al., J. Aerosol Sci., 1996, 27, pp. 951 and Y. Xiong et al., 1996, Combustion and Flame, 107, pp. 85.).

10   Many attempts have been made at controlling the phase of fine powders in a flame by optimizing process conditions or adding dopant materials, since the phase stability of many materials strongly depend on the temperature of and impurity, defects and strain existing in the particles. As an example, to obtain thermodynamically stable phase, high flame temperature conditions are favored,

15   however, under these conditions, particles become considerably larger.

Disclosure of the Invention

To solve the above problems, it is an objective of the present invention to provide a method of manufacturing spherical nanoparticles at high concentration and

20   also controlling the phase of the particles by irradiating a laser beam into a flame to obtain fine particles containing ceramic particles, metallic particles, glass particles or composite particles and deposit the fine particles for manufacturing an optical device base material by the flame.

Accordingly, to achieve the above objective, there is provided a method of

25   manufacturing fine particles including metallic particles, ceramic particles, glass particles or composite particles, comprising the steps of: supplying particle-forming reactants into a flame formed in a burner; generating particle nuclei from the reactants, which form aggregates by colliding with each other in the flame; and irradiating at least one laser beam into the aggregates in the flame so that the

30   temperature of the aggregates rapidly increases and the aggregates are fused and sintered into fine particles in the flame.

Here, the wavelength of the laser beam coincides with the main absorption wavelength band of the particles generated in the flame.

According to another aspect of the present invention, there is provided a method for depositing fine particles including metallic particles, ceramic particles, glass particles or composite particles on a target preform, the method comprising the steps of: supplying particle-forming reactants into a flame formed in a burner; generating particle nuclei from the reactants, which form aggregates by colliding with each other in the flame; irradiating at least one laser beam into the aggregates in the flame so that the temperature of the aggregates rapidly increases and the aggregates are fused and sintered into fine particles in the flame: and adhering the sintered particles to the preform to be deposited thereon.

Brief Description of the Drawings

The above objective and advantages of the present invention will become more apparent by describing in detail a preferred embodiment thereof with reference to the attached drawings in which:

FIG. 1 is a schematic diagram illustrating a conventional fine particle manufacturing apparatus;

FIGS. 2A and 2B illustrate particle growth mechanisms in a flame shown in FIG. 1;

FIG. 3 is a diagram for explaining a conventional method of manufacturing fine particles in order to control the growth of particles;

FIG. 4 is a diagram for explaining another conventional method of manufacturing fine particles in order to control the growth of particles;

FIG. 5 illustrates a fine particle manufacturing mechanisms according to the present invention;

FIGS. 6A through 6C illustrate examples of laser beams which can be employed in apparatus for performing a method of manufacturing fine particles according to the present invention;

FIG. 7 is a diagram showing a detailed embodiment of an apparatus for performing a method of manufacturing fine particles according to the present

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invention;

FIGS. 8A and 8B illustrate the distribution of temperatures in a flame according to the fine particle manufacturing method of the present invention;

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FIGS. 9A and 9B are graphs illustrating the scattered intensity with respect to the incidence position of a laser beam, according to the fine particle manufacturing method of the present invention;

FIG. 10 is a graph illustrating the weight fraction of the Rutile phase with respect to the collection position, in the absence of CO_2 laser irradiation;

FIG. 11 is a graph illustrating the variation of X-ray diffraction patterns of samples of powder collected at a height of 65 mm when the power of the CO_2 laser beam is irradiated at a height of 35 mm from the burner end, according to the fine particle manufacturing method of the present invention; and

FIG. 12 is a graph illustrating weight fractions of the Rutile phase for different incidence positions of a laser beam, according to the fine particle manufacturing method of the present invention

Best mode for carrying out the Invention

A method of manufacturing fine particles according to the present invention and a method of manufacturing an optical device preform can be performed by using a conventional apparatus shown in FIG. 1. The feature of the present invention lies in that a laser beam having a predetermined wavelength is irradiated when particles 6' are produced in a flame 5 at an end of a burner 4, as shown in FIG. 5.

According to the present invention, fine spherical powder particles and an optical device preform are manufactured as follows. Using the apparatus shown in FIG. 1, hydrogen and oxygen are introduced to the burner 4 to form a flame 5 and reactants are sprayed from the central part of the burner 4 into the flame using nitrogen or oxygen. Then, vapor reactants sprayed into the flame 5 react with each other to form particle nuclei of about 0.5 nm near the end of the burner 4. These nuclei move along the flame 5 to form very small-sized aggregates by collision. At this stage, if a laser beam having a wavelength close to the range of main absorption wavelengths of produced particles is irradiated with an appropriate power level, the temperature of the particle rapidly increases so that the small-sized aggregates completely coalesce to be turned into small-sized spherical particles 6' of about 5 to

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10 nm. That is to say, fine spherical particles are produced.

As stated in formula (1), the collision time decreases in an order of $T^{-1/2}$ as the temperature increases. However, the coalescence time decreases exponentially, that is, much faster than the collision time, according to the increase in the
5   temperature. Thus, if the particle temperature is sharply raised by irradiating a laser beam in the wavelength range in which particles readily absorb the laser beam into the tiny aggregates at an initial nucleation stage, coalescence of particles dominantly occurs, thereby generating small-sized spherical particles. Also, if the raised temperature of the particles is lower than their melting point, thermodynamically
10   stable phase can be obtained due to additionally supplying energy required the phase transformation to stable phase by irradiating the laser beam. If the laser power is high enough to melt the particles, a metastable phase can be obtained because the metastable phase are favored during recrystallization form liquid phase to solid phase due to short residence time in a flame.

15   In manufacturing an optical fiber preform using the thus-produced fine powder particles, a target substrate 10, for example, a silica rod, is spaced 10 to 20 cm apart from the end of the burner 4 to then be rotated at a speed of about 60 rpm, thereby depositing particles of 10 to 40 nm in size on the target substrate 10. Here, since the spherical particles have a much smaller collision area than the uncoalesced
20   aggregates (see S.E. Pratsinis, 1998, Prog. Energy Combust. Sci., 24, pp. 197-219.), the spherical particles exhibit lower collision rate while moving along the flame. Thus, immediately before deposition, the particles become much smaller-sized spherical particles (6' of FIG. 5) compared to the those (6 of FIG. 4) without laser incidence. This means that the coalescence rate can be controlled independently
25   of the collision rate, small-sized spherical particles can be produced even with an increase in the amount of a reactant carrier gas, and the deposition rate, quality of fine particles and optical device manufactured can be greatly improved. Deposition is consistently performed while a burner is moved left and right in the range of 1 m at a speed of 15 cm/min.

30   In manufacturing a planar optical wave guide or film, a silicon wafer having a diameter of about 12 inches, instead of a silica rod, is installed and particles are

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deposited while rotating and moving the wafer.

In separately manufacturing only the powder including ceramic, metallic and composite fine powder, instead of the target substrate 10, a ceramic filter or an electrical dust collector is installed to collect the particles produced in the above-
5   described process.

A laser beam can be made incident into a flame in various manners, as shown in FIGS. 6A through 6C. In addition to single incidence (FIG. 6A), which is simplest, multi-incidence of a laser beam is preferably employed, as shown in FIG. 6B, in order to enhance a laser incidence efficiency. In this case, a plurality of laser
10   beams may be irradiated. Also, laser beams may be cross-irradiated into a flame 5 by installing a plurality of mirrors 41 and 42. Alternatively, as shown in FIG. 6C, co-axial incidence in which a laser beam is irradiated coaxially with the flame 5 may be employed. Reference numerals 51, and 31 and 52 denote a mirror, and lenses for focusing a laser beam, respectively.

15   Compared to single incidence, multi-incidence allows effective utilization of laser energy by irradiating a laser beam several times in accordance with the movement of particles. According to the co-axial incidence, since particles consecutively absorb laser beams while moving along a flame by irradiating a laser beam through a transferring conduit of reactants in the burner, the same effect can
20   be exerted with a low power laser.

The inventors carried out the following experiment to prove the actual effect of the present invention.

EXAMPLE

25   The reactant supplying apparatus and a fuel flow controlling apparatus were installed in the same manner as in FIG. 1. As shown in FIG. 7, a flame stabilizer 4b such as a honeycomb structure was additionally installed at the outside of a coflow diffusion flame burner 4 consisting of four stainless steel tubes to form a stable laminar diffusion flame. A mixed gas of $SiCl_4$ and N_2 was supplied to the central
30   part of the burner 4 through a nozzle 4a. In order to prevent the nozzle 4a from clogging due to particles produced at the outlet of the nozzle 4a, nitrogen for

shielding was injected through a plurality of holes formed around the nozzle 4a.

In FIG. 7, 61a through 61c denote polarizers, 62a through 62c lenses, 82 laser line filters, 63a and 63b pinhole openings, 64 a mirror, and 91a and 91b beam dumps.

5   Also, a CO_2 laser 70 was installed a predetermined distance (referred to as h_L) above from the end of the burner 4 to irradiate a laser beam, and an Ar ion laser 60 was installed 5 mm above the CO_2 laser 70 to irradiate a laser beam having a wavelength of 514 nm. Then, scattered light signals produced by particles were stored in a personal computer (not shown) through a photomultiplier tube (PMT) 80.

10   Also, the particles were thermophoretically sampled at the same height as the Ar ion laser beam and particle size and morphology were measured by transmission electron microscopy (TEM) to then be compared with scattered light intensity, thereby verifying how effective CO_2 laser beam incidence is in controlling the growth of particles produced in the flame. The Ar ion laser 60 was installed predetermined

15   distance, i.e., a sampled position (referred to as hp) above the end of the burner 4 and 5 mm above the CO_2 laser 70.

The scattered intensity measured in either direction with respect to aggregate-like particles is proportional to a value obtained by Formula (3) (see R.A. Dobbins et al., 1991, Applied Optics, 30 (33), pp. 4747-4754.):

20    $$N\overline{n^2}x_p^{\ 6}f(q^2\overline{R_g^{\ 2}})\ ...(3)$$

where N is the number density of aggregates, n is the number of primary particles, x_p is the ratio of a primary particle diameter (d_p) to a wavelength (λ) of laser beam, i.e., $\pi\, d_p/\lambda$, and R_g is the radius of gyration of an aggregate, indicating how far primary particles are spaced apart from the mass center of the aggregate. As

25   expressed in Formula (3), the scattered intensity increases in proportion to the primary particle diameter (d_p) raised to the sixth power and the number density of aggregates. Thus, based on the assumption that the number density of particles is not greatly changed according to the magnitude of the measured scattered intensity, a change in the particle size can be qualitatively estimated. Also, particles are

30   thermophoretically sampled at local spots in a flame and the particle size and the change in the morphology can be quantitatively identified by TEM.

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In order to maximize the effect of a CO_2 laser beam, it is necessary to know changes in terms of size or morphology with a change in the flame temperature and then to derive the proper incidence position of a laser beam. While varying the distance hp, the radial distribution of the flame temperature was measured using a B-

5   type thermocouple. Here, once particles are produced, since the particles are adhered to the thermocouple, it is impossible to measure the temperature. Thus, only nitrogen (N_2) was injected at the same flow rate as the total flow rate of the carrier gas injected through a nozzle to measure the temperature under the same conditions as those when producing particles. The diameter of a thermocouple bead was 0.5

10   mm, and the distribution of the flame temperature, which was based on the correction due to radiation and convection, is shown in FIG. 8A. When the distance hp was set to be less than 11 mm, a low temperature was measured at the center of the flame. However, at a position of about 5 mm away from the center of the flame (x=0), the flame temperature was 2000 °C or above. The low temperature at the flame center

15   is caused by a cooling effect of the flame due to a shield gas injected for preventing the produced particles from adhering to the surface of the nozzle. Also, the distance hp gets higher value, the maximum points of flame temperatures move toward the center of the flame, that is, toward a point where x=0 mm. At hp distances of 17 mm or higher, which are indicated by -•-, -▲- and -▼- in FIG. 8A, the flame

20   temperature distributions are parabola-shaped. This is caused by diffusion of oxygen and hydrogen in the flame. Since the chemical reaction of $SiCl_4$ is dependent on the temperature, the produced particle distribution is similar to the distribution of the flame temperature, and it was verified through light scattering experiment that the particle distribution was similar to the distribution of scattered light signals.

25   FIG. 8B shows the gas heating effect due to a CO_2 laser beam, which is verified by observing a change in the temperature using a thermocouple at positions of hp =11, 20 mm, which is 5 mm above a CO_2 laser, when a 1137 Watt (W) CO_2 laser beam was irradiated at positions of h_L = 6 mm and 15 mm away from the end of the burner. In the flame, hydrogen, oxygen and nitrogen induced into the flame,

30   moisture vapor and intermediate products generated by combustion of hydrogen, and the like are present. Presumably, the gas temperature is raised by about 100 °C due

to laser absorption of the intermediate products generated by the combustion of hydrogen. At a position of hp = 11 mm, laser absorption by gas was relatively small and a relatively small increase in the gas temperature, that is, about 40°C, was shown, which was because the concentration of injected nitrogen was high and

5   hydrogen was not sufficiently diffused at the center of the flame. The infrared absorption bands of SiO_2 are 455 cm^{-1}, 1090 cm^{-1} and 800 cm^{-1} (see R. A. Nyquist et al., Infrared Spectra of inorganic compounds, 4, Academic Press, Inc., 1997.). Also, the frequency of the CO_2 laser beam is 934 cm^{-1}, at which frequency coincidence occurs more easily in particles than the case of the gas. Further, the size

10   of a particle is at least 100 times greater than the size of a gas molecule. Thus, the actual laser absorption of particles is much larger than that of the gas. Laser beam incidence into particles results in a sharp increase in the particle temperature compared to in the gas temperature.

While gradually increasing the intensity of the CO_2 laser beam with 0 W, 266

15   w, 750 w, 1150 W and 1490 W and varying the incidence position (h_L) from 5 mm to 19 mm (that is, varying hp from 10 mm to 24 mm, as indicated on the horizontal axes of the graphs shown in FIGS. 9A and 9B), a change in the scattered intensity was observed along the center of a flame with respect to the carrier gas flow rates of 50 sccm and 150 sccm, which are shown in FIGS. 9A and 9B, respectively, in which

20   the horizontal axes indicate scattered intensity measuring positions (hp), and a CO_2 laser was irradiated into the flame at a position 5 mm lower than hp. In FIG. 9A, in the case where the CO_2 laser was not irradiated, that is, I=0, the scattered intensity increased monotonically as the hp distance increased

The scattered intensity sharply increased up to approximately 14 mm in the

25   hp distance due to rapid nucleation and coagulation, which are caused by chemical reactions, while the scattered intensity gently increased at a position of over 14 mm. However, laser incidence makes a quite different tendency in the scattered intensity variation.

Since chemical reaction of $SiCl_4$ occurs incompletely below 9 mm near the

30   center line of the flame, CO_2 laser incidence causes a chemical reaction by an increase in the gas temperature by a laser beam, as shown in FIG. 8B, thereby

producing particles. Thus, the scattered intensity was increased 5 mm above the CO_2 laser beam, that is, hp $\leq$ 14 mm, as shown in FIG. 9A. As the power of the CO_2 laser increased, the efficiency of producing particles was enhanced. At a position 9 mm higher than and 14 mm lower than the end of the burner, where particles grow

5   rapidly even with termination of chemical reactions, aggregates due to collision, coagulation and coalescence of produced particles are present. Here, if a CO_2 laser beam is irradiated, primary particles constituting the aggregates absorb the CO_2 laser beam and are then sintered to produce small spherical particles. Also while the particles move along the flame, collision cross sections decrease, thereby suppressing

10 the formation of aggregates. Accordingly, the scattered intensity (in FIG. 9A, 14 mm $\leq$ hp $\leq$ 19 mm) decreases with an increase in the CO_2 laser power. When the CO_2 laser beam is irradiated at a position of 14 mm away from the end of the burner, that is, when hp = 19 mm, the minimum scattered intensities were observed with respect to the respective power levels. At a position of 15 mm or higher, spherical

15 particles which have already been sintered were formed, and incidence of the CO_2 laser beam caused an increase in the absorption efficiency of the laser beam. This is because the size of a spherical particle is much larger than that of a primary particle in the cluster. Thus, the spherical particles were evaporated and the scattered intensity thereof was decreased as the CO_2 laser power increased. The

20 evaporated gaseous particles are cooled by heat exchange with surrounding gas molecules immediately after they are applied to the CO_2 laser, and are then recondensed. During recondensation, aggregates are unavoidably produced due to homogeneous nucleation and a large numbers of particles. In the case where the flow rate of the reactant carrier gas was increased to 150 sccm, the change in the scattered

25 intensity with CO_2 laser incidence is shown by hp distance in FIG. 9B in the same manner as in FIG. 9A.

Referring to FIGS. 9A and 9B, as the flow rate of a carrier gas increases, the incidence position at which the effect of the CO_2 laser incidence is largest, that is, the minimum point of the scattered intensity is shifted from 14 mm (that is, hp = 19 mm)

30 to 17 mm (that is, hp = 22 mm), that is, the minimum scattered intensity position gets further from the end of the burner as the flow rate of a carrier gas increases. Also,

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it was understood that the particle generation effect induced by irradiating a laser beam to a low position was reduced as the flow rate of the carrier gas increases. In this experiment, in order to keep a constant time for a particle to pass through a CO_2 laser beam even with a change in the flow rate of the carrier gas, the total flow rate

5   of N_2 as the carrier gas, $SiCl_4$ and additionally added N_2 was maintained constantly by adjusting the flow rate of the additionally added N_2 gas. Thus, the speed of the particles and gases are almost the same with the lower gas flow rate case. However, since $SiCl_4$ injected through a nozzle is 20 times or more heavier than nitrogen, an increase in the flow rate of $SiCl_4$ increases and the momentum thereof at the outlet

10   of the nozzle increases, which slows down the diffusion of hydrogen. Thus, the temperature of the center of a flame decreases and the chemical reaction thereof is retarded accordingly. Also, as the flow rate of $SiCl_4$ increases, the number density of the particles increases and a larger aggregate consisting of smaller primary particles is produced due to an increased collision frequency. Further, the position

15   at which the aggregate is completely sintered and then is changed into spherical particles also moves upwards as the flow rate of $SiCl_4$ increases.

In the same context, the minimum point of the scattered intensity of FIG. 9A moves upwards in FIG. 9B, as the flow rate of $SiCl_4$ increases.

In order to verify the particle generation effect at a low position, the particle

20   sintering effect at a minimum point of the scattered intensity and the particle evaporation effect at a high position with a low flow rate of a carrier gas, as shown in FIG. 9A, a CO_2 laser beam was irradiated at 6mm, 12mm and 18mm, and then particles were sampled at 11mm, 17mm and 23mm and observed.

First, there is no CO_2 laser incidence, that is, I equals 0 W, gases are mostly

25   present at a position of 6 mm and particles start being generated from a gaseous phase at 11 mm which is the sampling position. In this case, an increase in the power of CO_2 laser beam incidence causes an increase in the particle generation effect.

In the case where the incidence position of a laser beam was 12 mm and the

30   sampling position was 17 mm, the particle size was reduced from approximately 70 nm to approximately 40 nm while maintaining spherical shapes, as the CO_2 laser

power increases.   Also, when I equals 1170 W, due to evaporation and recondensation, very small particles of 5 nm in diameter were adhered to the surfaces of particles.   In other words, it was verified that laser incidence into a flame satisfactorily changed the particle size.

5   On the other hand, since completely sintered spherical particles were present at the high flame heights and no further sintering occurred with CO_2 laser incidence and evaporation occurred on the particle surface instead at 18 mm, no considerable change in the size of spherical particles could be observed, even when the power of the laser was increased. When I equals 1808 W, which is a considerably high power

10   level, it was seen that the spherical particle size was slightly reduced and a large amount of aggregates consisting of very small particles due to evaporation and recondensation were present.

Also, particles was sampled at a position of 20 mm when the incidence position of a laser beam is 15 mm at a high flow rate of a carrier gas (150cc/min).

15   When I equals 0 W, partially-sintered aggregates seen immediately before being completely sintered were observed. Even with a low laser power level of 260W, the aggregates were sintered, thereby producing perfectly spherical particles. When the laser power was increased, the particles became smaller by about 60% while the shapes of the particles were still spherical. This is quite an encouraging result in

20   terms of deposition rate. If the flow rate of a carrier gas is increased to about 3 times, the deposition rate linearly increases and thus small-sized spherical particles can be produced for deposition, which is in conformity to the objective of the present invention. Also, if the absorption wavelength of produced particles coincide with or is close to the frequency of the irradiated laser beam, the effect of manufacturing fine

25   particles can be considerably increased by low power laser incidence.

For further confirmation of the above effect of CO_2 laser irradiation and another effect of the present invention, that is, keeping the fine powders in the solid-state, the inventors applied this control method to TiO_2 particles. All experimental apparatuses except for the reactant materials were the same as those of the previous

30   experiment.   Here, $TiCl_4$ was used for reactant material and had much lower saturated vapor pressure than $SiCl_4$, therefore, the bubbler 1a in FIG. 1 was

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maintained at a higher temperature of 40 °C than that of $SiCl_4$. TiO_2 powders were generated in the oxygen-hydrogen diffusion flame via hydrolysis of $TiCl_4$ and deposited on a quartz tube (6mm in diameter) which was cooled by flowing water through the tube. The deposited powders were collected for measurement of X-ray

5   diffraction (XRD) for CuK α radiation.

TiO_2 particles are known to have three solid-state phases of anatase, brookite and rutile. Rutile is the only thermodynamically stable phase, whereas the others are metastable phases. Anatase is the most common product of low-temperature synthesis pathways and is an important component of nanocrystalline materials

10   developed for gas-phase separation and catalysis (Amores et al., 1995, J. Materials Chem., 5, pp. 1245-1249). Rutile content in TiO_2 particles was determined from the relative X-ray diffraction intensity corresponding to Anatase <101> and Rutile <110> reflection. Weight fraction of rutile becomes:

$$M_R/(M_A + M_R) = 1/(1 + K_c I_A/I_R)$$

15   where M denotes weight, I denotes measured intensity, K_c is given as 1.26 by Spurr and Myers (1957, Anal. Chem., 29, pp. 760), subscript R corresponds to Rutile and subscript A corresponds to Anatase.

The scattered intensity was also varied with the power level and irradiation position of CO_2 laser, which was considerably similar to that of SiO2. When a CO_2

20   laser beam was irradiated at the suitable position where small aggregates existed, scattered intensity become decreased with increasing CO_2 laser power and the particles were also changed from a large aggregate to smaller spherical particles whose average diameters were less than 30 nm.

Because the activation energy for transformation from Anatase to Rutile is of

25   the order of 400kJ/mol (Mackenzie, 1975, Trans. J. Brit. Ceram. Soc., 74, pp. 77), the weight fraction of Rutile is presumed to increase with increasing the flame temperature or the residence time in a flame. Therefore, rutile weight fraction was increased as the collecting position of the particles moved upward along the flame for the case without irradiation of CO_2 laser beam, as shown in FIG. 10. The other

30   factors which affect the phase transformation may be the time that an aggregate remains small in size and the degree of structural imperfection in the aggregate, that

is, defects in the TiO_2 particles composed of oxygen vacancies (Suyama et al., 1975, J. Inorg. Nucl. Chem., 37, pp. 1883) and the amount of micro-strain in TiO_2 particles. Since anatase particles below 14nm in size are thermodynamically stable due to size effect, anatase phase was more favored near the burner surface than rutile

5   phase. However, as a sampling height becomes higher, anatase particles were grown. Then, rutile phase becomes more stable and rutile nuclei occurred mainly around necks between primary particles in an aggregate. Therefore, rutile contents increased with the sampling height.

In the same context, rutile weight fraction was easily expected to be increased

10   with increasing CO_2 laser power, whereas CO_2 laser irradiation gave the contrary result. FIG. 11 shows the variation of X-ray diffraction patterns of TiO_2 powders collected at a height of 65mm when the power of the CO_2 laser beam is irradiated at a height of 35mm from the burner end. In the picture, A denotes anatase and R denotes rutile. Surprisingly, rutile contents were found to be slightly increased and

15   then decreased with increasing CO_2 laser power. This could be explained by the possibility of melting the TiO_2 nano particles by irradiating CO_2 laser beam on particles generated in a flame. Rutile can not be reversibly transformed to anatase in solid phases and rutile weight fraction was about 13% at 35mm (see Fig. 10). Decrease in the rutile weight fraction below 13% could be explained only by melting

20   the particles since anatase phase first appeared during recrystallization from liquid phase to solid phase. In FIG. 12, at all CO_2 laser irradiation positions, the similar tendency was found. If the raised temperature of the particles is lower than their melting point, thermodynamically stable phase, that is, rutile weight fraction should be increased due to additionally supplying energy required for the phase

25   transformation into a stable phase by irradiating a laser beam. Otherwise, if the laser power is high enough to melt the particles, a metastable phase, anatase phase should be dominant since the metastable phase are favored during recrystallization from liquid phase to solid phase due to the short residence time in a flame. In this way, the laser irradiation in a flame in the present invention can be used to control phase

30   of nano crystalline particles.

As described above, according to a method of manufacturing fine particles

and a deposition method thereof of the present invention, a laser beam is irradiated into particles produced in a flame to facilitate sintering of the produced particles, thereby obtaining spherical nanoparticles at high concentrations, controlling the phase of the particles and improving the quality of the produced particles and the quality

5   of a thin film formed by depositing the produced particles. ·

Industrial Applicability

Although the invention has been described using an exemplary preferred

10   embodiment, various modifications and changes can be effected by one skilled in the art within the scope of the present invention, and it is intended the scope of the invention be defined by the claims appended thereto. In other words, it is to be understood that the invention is applicable to general processes of manufacturing fine particles in a flame, including crystalline or non-crystalline particles and films.